926,902

PATENT SPECIFICATION

NO DRAWINGS

926,902

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COMPLETE SPECIFICATION

Improvements in or relating to Fluidifying Agents for Synthetic Resin Dispersions

We, PECHINEY COMPAGNIE DE PRODUITS CHIMIQUES ET ELECTROMETALLURGIQUES, a French Body Corporate, of 23, Rue Balzac, Paris 8e, France, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is concerned with improving the flow properties of plastisols of vinyl chloride solid polymers suspended in plasticisers therefor.

Various other ingredients, for example, stabilisers, fillers, pigments and colouring agents, also in suspension in the plasticiser, may be also present in the plastisols which have numerous industrial applications. The commonest applications are the coating of papers or fabrics and, in general, the covering of articles or materials by dipping, casting or any other appropriate means. The plastisols are also used to produce, by moulding, solid or hollow articles having the appearance of rubber.

The applications of these plastisols depend very largely upon their flow properties, particularly their possession of a minimum flow stress, thixotropy, viscosity for a given speed gradient and variation of viscosity as a function of the speed gradient.

The main factors which influence these flow properties are:

(a) the chemical nature and the physical state of the polymer and of the various ingredients accompanying it;

(b) the nature of the plasticiser or plasticisers employed;

(c) the concentrations of the polymer of the plasticisers and of the various ingredients in the suspension;

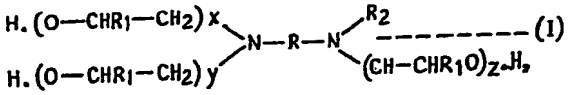
(d) the ageing of the suspension as shown by an increase in viscosity which takes place as a function of time; this occurs more rapidly as the temperature increases, probably owing to a slow gelatinisation at room temperature.

Excessive viscosity of the plastisols causes difficulties in the use of these products, and various efforts have been made to reduce it.

According to our invention we provide a plastisol of a vinyl chloride polymer suspended in a liquid plasticiser which plastisol contains a proportion within the range of from 0.1% to 5% by weight, inclusive, based on the dry weight of the polymer present, of a fluidifier which is a condensation product of ethylene oxide or propylene oxide with an aliphatic diamine whose aliphatic radical is saturated or unsaturated, is a straight-chain or branched-chain radical and contains between 2 and 30 carbon atoms, inclusive, the condensation product being in the form of a free amine, or of the fatty acid salt of the free amine.

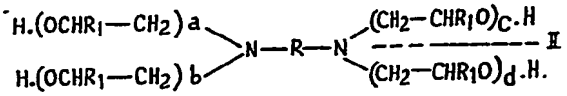
We have found by practical tests that the fluidifiers in accordance with our invention considerably lower the viscosity of the plastisols, and this lowering is well retained during the course of ageing. Even after storage for a week or two at about 20°C., the plastisols in which these fluidifiers have been incorporated are distinctly less viscous than those which do not contain such fluidifiers.

Our fluidifiers include compounds of the following general formulae, and their fatty acid addition salts:



(1)

and



II

In the above formulae, the symbols have the following meanings:

R represents a saturated or unsaturated straight-chain or branched chain aliphatic group in which the number of carbon atoms may vary from 2 to 30; this number is, however, preferably 2, 3, 4 or 6;

R_1 is either hydrogen or a methyl group, depending upon whether ethylene oxide or propylene oxide is used to form the condensation product;

a, *b*, *c*, *d*, *x*, *y* and *z* are equal or different integers which may range from 1 to 30, but which are preferably between 5 and 12; and

R_2 is a saturated or an unsaturated, straight-chain or branched aliphatic group chain, in which the number of carbon atoms may vary from 5 to 30, but is preferably between 14 and 18.

These fluidifiers may be added to the mixture being treated at the time of the preparation of the plastisol. Alternatively, they may have previously been mixed with one of the constituents of the plastisol. The diamines dissolve readily in most plasticisers for vinyl chloride polymers and can conveniently be introduced into the mixture in this form.

The fluidifiers may also be incorporated with the fillers, pigments and colouring agents used, either directly or in the form of a solution in a volatile solvent which is subsequently eliminated.

Since the polymers used in the plastisols are generally specially prepared for this use, it is convenient to introduce the fluidifiers into them in the calculated quantity, so that the user can effect the mixing with the plasticiser and with the ingredients used without having to concern himself with the addition of the fluidifier.

The incorporation of the fluidifier into the polymer may take place in the course of the polymerisation of the monomer. The amine is then introduced into the autoclave either in the free state or in the form of a salt of a fatty acid, e.g. a laurate or a stearate.

It is also possible to add the fluidifier to the latex which is obtained after polymerisation, or again it may be incorporated in the dry polymer in the course of the crushing of the latter, either directly or in the form of a solution in a volatile solvent which is subsequently eliminated.

Proportions of fluidifier between 0.5% and 2% dry weight based on the dry polymer generally give the best results.

Since the fluidifiers of the invention are substantially non-volatile, they remain in the polymer gel when the plastisol is brought to its gelatinisation temperature. This is an advantage, because they perform the function of a stabiliser against the action of heat in the course of the gelatinisation of the plasticised mass.

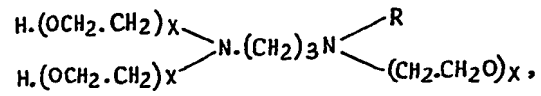
The following examples are representative of the invention. They are concerned with the influence of various fluidifiers representative of the invention on a plastisol which is composed of 40% by weight of neutral ethylhexyl phthalate, commonly known as D.O.P., and 60% of polyvinyl chloride which has been specially prepared for this use.

The viscosity of the pastes obtained was measured in all cases at 25°C., using a DRAGE viscometer ("DRAGE" being a Swiss Trade Mark), the moving element of which is in the form of a cross and rotates at a speed of 200 r.p.m.

The viscosity variation as a function of time was observed on two specimens in each case, one being kept at 20°C. and the other at 30°C. The results of the viscosity measurements are given in centipoises and the percentages are by weight.

EXAMPLE I

Two fluidifiers with structures corresponding to formula I above were successively employed. The fluidifiers had been prepared by the condensation of ethylene oxide with a substitution product of trimethylene diamine yielding compounds of the structure:



R indicating a saturated straight chain containing from 14 to 18 carbon atoms and x being equal to 3 and 7 respectively; the fluidifiers were given the references D_3 and D_7.

Each fluidifier was dissolved in the plasticiser before the latter was mixed with the vinyl chloride monomer.

The following results were obtained, the figures at the right hand side of the table being the viscosities in centipoises at 25°C.

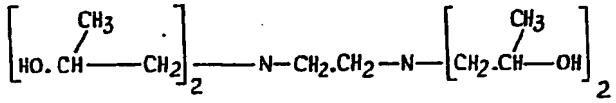
TABLE I

Keeping temperatures of the pastes	Fluidifier	Percentage of fluidifier in proportion to the resin	Elapsed Time			
			½ hour	1 day	8 days	15 days
20°C.	0	0	10,900	15,500	16,100	17,000
30°C.			10,900	19,700	24,000	
20°C.	D_3	0.5	6,400	8,900	13,200	14,900
30°C.			6,400	16,200	22,800	24,000
20°C.	D_7	0.5	5,400	8,500	12,200	15,000
30°C.			5,400	14,000	21,000	24,000

Apart from the viscosity variations indicated in this table, it is to be noted that the standard paste, even when freshly prepared, does not flow by itself, while in the presence of the fluidifier these pastes flow with much greater readiness than is suggested by the viscosity difference after 8 days, for example.

EXAMPLE II

The fluidifier employed was N,N,N¹,N¹-tetrahydroxypropyl ethylene diamine:



which had been obtained by condensing propylene oxide with dimethylene diamine.

This product, which was given the reference N_3, was dissolved in the plasticiser before the latter was mixed with the polyvinyl chloride powder. The following results were obtained, the figures at the right-hand side of the table being the viscosities in centipoises at 25°C.

TABLE II

Keeping temperatures of the pastes	Percentage of fluidifier in proportion to the resin	Elapsed Time				
		½ hour	1 day	4 days	10 days	15 days
20°C.	0	6,000	5,400	10,200	11,600	13,100
30°C.		6,000	15,000	17,800	24,000	
20°C.	0.5	3,600	6,000	7,500	8,400	9,600
30°C.		3,600	10,500	15,000	17,600	23,000
20°C.	2	3,000	5,500	6,300	7,100	7,100
30°C.		3,000	8,600	13,800	16,800	20,200

It will be seen that this product has a remarkable effect on the fluidity of the paste, and that the plastisol effectively resists ageing at room temperature.

EXAMPLE III

Two of the fluidisers employed in the preceding Examples were incorporated in pastes prepared with a poly-vinyl chloride which is sold for commercial pastes, namely "Geon 121," "Geon 121" being a Registered Trade Mark of the B.F. Goodrich Chemical Co.

As in the preceding examples, the fluidifiers were dissolved in the plasticiser (D O P).

Pastes containing 40% of the plasticiser and 60% of Geon 121 were prepared. When tested as above the following results were obtained, the figures at the right-hand side of the table being the viscosities in centipoises at 25°C.

TABLE III

Keeping temperatures of the pastes	Fluidifier	Percentage of Fluidifier in proportion to the resin	Elapsed Time		
			½ hour	3 days	7 days
20°C.		0	5,800	8,600	9,400
30°C.			5,800	17,700	17,700
20°C.	D7	0.5	4,300	7,700	8,200
30°C.			4,300	14,700	14,700
20°C.	N4	0.5	5,200	8,000	8,500
30°C.			5,200	15,300	15,300

"Geon 121" is a special polyvinyl chloride for plastisols, which already contains as a fluidifier 2% of a fatty alcohol fraction containing from 10 to 14 carbon atoms. The foregoing table shows therefore that the products of the present invention can further improve a plastisol which already contains a fluidifier.

EXAMPLE IV

Two of the fluidifiers appearing in the foregoing examples (D7 and N4), were dissolved in various fractions of the same latex of a polyvinyl chloride to produce pastes with a concentration of 0.5% of the fluidifier, calculated on the weight of the polymer, and the paste was then atomised. Pastes containing 40% of plasticiser and 60% of resin were employed. When tested as above, the following results were obtained, the figures at the right-hand side of the table being the viscosities at 25°C. in centipoises.

TABLE IV

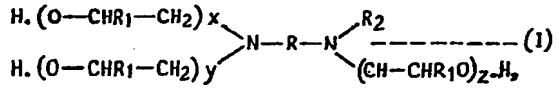
Keeping temperatures of the pastes	Fluidifier	Elapsed Time			
		½ hour	1 day	7 days	15 days
20 °C.	nil	5,600	10,700	11,400	11,600
30 °C.		5,600	17,300	19,400	21,000
20 °C.	D7	4,900	6,300	8,000	9,400
30 °C.		4,900	11,200	16,000	17,900
20 °C.	N4	3,200	8,000	9,300	9,300
30 °C.		3,200	13,800	15,000	21,000

The fluidifying effect is particularly marked in the initial stages, while it is also appreciable after storage for one or two weeks.

WHAT WE CLAIM IS:—

1. A plastisol of a vinyl chloride-polymer suspended in a liquid plasticiser which plastisol contains a proportion within the range of from 0.1% to 5% by weight, inclusive, based on the dry weight of the polymer present, of a fluidifier which is a condensation product of ethylene oxide or propylene oxide with an aliphatic diamine whose aliphatic radical is saturated or unsaturated, is a straight-chain or branched-chain radical and contains between 2 and 30 carbon atoms, inclusive, the condensation product being in the form of a free amine or of the fatty acid addition salt of the free amine.

2. A plastisol as claimed in Claim 1 in which the fluidifier has the formula:



(I)

in which:

R represents the aliphatic radical defined in Claim 1;

R_1 represents H or CH_3;

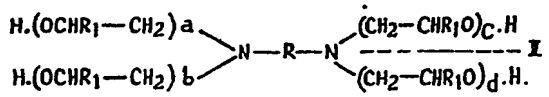
R_2 represents a saturated or unsaturated, straight-chain or branched-chain aliphatic group of between 5 and 30 carbon atoms, inclusive; and x, y and z are equal or different integers which range from 11 to 30, inclusive; or is the fatty acid addition salt of the free amine of formula (I).

3. A plastisol as claimed in Claim 2 in which R has 2, 3, 4 or 6 carbon atoms.

4. A plastisol as claimed in Claim 2 or 3 in which x, y and z range between 5 and 12, inclusive.

5. A plastisol as claimed in any of Claims 2 to 4 in which R_2 has between 14 and 18 carbon atoms, inclusive.

6. A plastisol as claimed in Claim 1 in which the fluidifier has the formula:



(II)

in which:

R represents the aliphatic radical defined in Claim 1;

R_1 represents —H or —CH_3; and

a, b, c, and d are equal or different integers which range from 1 to 30, inclusive; or is the fatty acid addition salt of the amine of formula (II).

7. A plastisol as claimed in Claim 6 in which R has 2, 3, 4 or 6 carbon atoms.

8. A plastisol as claimed in Claim 6 or 7 in which a, b, c and d range from 5 to 12, inclusive.

9. A plastisol as claimed in any of the preceding Claims in which the fluidifier is present in the suspension in a proportion within the range of from 0.5% to 2%, inclusive by weight, based on the dry weight of the polymer.

10. A plastisol as claimed in any of Claims 1 to 9 in which the plasticiser is diethylhexylphthalate.

11. A plastisol as claimed in any of the preceding claims which contains one or more additional fluidifying agents.

12. A plastisol of a vinyl chloride polymer suspended in a liquid plasticiser as claimed in Claim 1, the plastisol being substantially as hereinbefore described.

13. A plastisol of a vinyl chloride polymer suspended in a liquid plasticiser as claimed in Claim 1, the plastisol being substantially as hereinbefore described with reference to any of the specific examples.

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